Secondary ion mass spectrometer analyses for trace elements in glass standards using variably charged silicon ions for normalization

ERIC N. CARLSON1,‡ and RICHARD L. HERVIG1,*†

1School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

Trace element analyses of silicate materials by secondary ion mass spectrometry (SIMS) typically normalize the secondary ion count rate for the isotopes of interest to the count rate for one of the silicon isotopes. While the great majority of SIMS analyses use the signal from Si⁺, some laboratories have used a multiply charged ion (Si³⁺ or Si⁴⁺). We collected data and constructed calibration curves for lithium, beryllium, and boron using these different normalizing species on synthetic basaltic glass and soda-lime silicate glass standards. The calibrations showed little effect of changing matrix when Si⁺ was used, but larger effects (up to a factor of ~2) when using Si³⁺ or Si⁴⁺ are a warning that care must be taken to avoid inaccurate analyses. The smallest matrix effects were observed at maximum transmission compared to detecting ions with a few tens of eV of initial kinetic energy (“conventional energy filtering”). Normalizing the light element ion intensities to Al³⁺ showed a smaller matrix effect than multiply-charged Si ions. When normalized to ¹⁶O⁺ (which includes oxygen from the sample and from the primary beam), the two matrices showed distinct calibration curves, suggesting that changing sputter yields (atoms ejected per primary atom impact) may play a role in the probability of producing multiply charged silicon ions.

Keywords: SIMS, lithium, beryllium, boron; Lithium, Beryllium and Boron: Quintessentially Crustal

INTRODUCTION

Secondary ion mass spectrometry (SIMS) is very sensitive to many elements, and the three light lithophile elements, lithium, beryllium, and boron, have represented a frequent application of this technique. There are many examples of the calibration of SIMS for these elements (e.g., Hervig 1996, 2002; Ottolini et al. 1993). These reports indicate that the variation in major element chemistry does not play a large role in changing the calibration factor (e.g., Ottolini et al. 1993; Dunham et al. 2020), although there are exceptions (de Hoog and EIMF 2018). That is, the effect of bulk chemistry on the ion yield of these elements at trace levels in “common” matrices tends to be small. Most SIMS calibrations involve normalizing the intensity of the ion of interest to a matrix ion, such as one of the silicon isotopes, when studying silicate minerals and glasses. The normalization is important because (at least in the Cameca IMS design) there is a very strong potential gradient between the sample and the grounded extraction lens, and if the distance between the sample and ground varies (resulting from using even slightly tilted samples or slightly deformed sample holders), the absolute count rates can change, while ion ratios (e.g., Li⁺/Si⁺) will vary less as the sample is moved to examine different areas [note that even the ion ratios may be significantly affected if tilting is excessive (Deng and Williams 1989)].

Some published results select secondary ions ejected with several tens of eV initial kinetic energy [the energy filtering approach (e.g., Shimizu and Hart 1982; de Hoog and EIMF 2018)] while other researchers have used the more intense, low-energy secondary ions (e.g., Marschall and Monteleone 2014; Dunham et al. 2020). In these and in most other applications to geological materials, the normalizing ion was typically singly charged silicon. However, silicon (like many other elements) will form multiply charged ions (such as Si²⁺, Si³⁺, and even Si⁴⁺), for which the signal shows up at mass/charge of 14, 9.3, and 7, assuming the most abundant isotope, ²⁸Si, is detected. One attraction of using, for example, the doubly charged ion is that the count rate decreases by a factor of a few thousand compared to the singly charged ion, allowing the operator to increase the primary beam current to remove more atoms of trace elements/isotopes and increase sensitivity while keeping the normalizing ion from saturating the electron multiplier (EM) detector. Using a different detector for Si (Faraday cup) than the trace elements in the analysis routine (electron multiplier) is an alternative, but might affect precision because of changing EM detector parameters (aging). Perhaps the most important reason to explore the effects of using multiply charged ions is that applications to light element (Li to B elemental and isotopic) analysis using large-geometry SIMS instruments typically involve collecting a signal for silicon using Si³⁺ or Si⁴⁺. This requires a smaller change in the magnetic field compared to monitoring singly charged silicon (see, for example, Dunham et al. 2020), thus reducing hysteresis effects on instruments with large magnets.

There is nothing intrinsically wrong with using multiply charged ions in SIMS analyses. For example, Ricciuti et al. (1993) asserted that calibrations for rare earth elements using...